UTILASATION OF A NATURAL ANTIOXIDANT FROM *ELAEIS GUINEENSIS* (OIL PALM) LEAVES IN RUBBER COMPOUNDS

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By

NOR HASMANIZA HUSNA BINTI SHUHAIMI

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DECLARATION

I declare that the content presented in this dissertation entitled **"UTILASATION OF A NATURAL ANTIOXIDANT FROM *ELAEIS GUINEENSIS* (OIL PALM) LEAVES IN RUBBER COMPOUNDS"** is own my work which was done at Universiti Sains Malaysia unless onformed otherwise. This dissertation has not been previously submitted for any other degree.

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam disertasi ini bertajuk **"KEGUNAAN ANTI-OKSIDA SEMULAJADI DARIPADA ELAEIS GUINEENSIS DAUN (KELAPA SAWIT) DI DALAM SEBATIAN GETAH ASLI"** adalah hasil kerja saya dan dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Disertasi ini juga tidak pernah disertakan untuk ijazah yang lain sebelumnya.

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Witness by,

Signature:

Supervisor's Name: **DR NADRAS OTHMAN**

Date:

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LIST OF ABBREVIATIONS

Abbreviation	Description
ADS	Air-Dried Smoke
ASTM	American Society for Testing and Materials
AU	Urethane Rubber
BHA	butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BR	Butadiene Rubber
CBS	N-cyclohexylbemzothiazole-2-Sulfenamide
CGNR	Cardanol Grafted Natural Rubber
CNSL	Cashew Nut Shell Liquid
CR	Chloroprene Rubber
CV	Conventional Vulcanization
ECO	Epichlorohydrin Rubber
ENR	Epoxidized Natural Rubber
EPDM	Ethylene-Propylene-Diene Rubber
EV	Efficient Vulcanization
FTIR	Fourier Transform Infrared Spectrometry
GC-MS	Gas Chromatography- Mass Spectrometry
IIR	Butyl Rubber
IR	Isoprene Rubber
KPS	Potassium Peroxydisulfate
MBS	N-oxydiethylene-2-benzothiazole Silphenamide
NA	Natural Antioxidant

NBR	Acrylonitrile-Butadiene Rubber
NCR	Acrylonitrile-Chloroprene Rubber
NIR	Acrylonitrile-Isoprene Rubber
NR	Natural Rubber
OPE	Oil Palm Leaves Extract
OT	Polyglycol Ether Rubber
OTOS	N-oxydiethylene Dithiocarbomyl N^1-oxydiethylene Sulphenamide
P2APy	Poly (2-aminoprydine)
PBR	Vinylpyridine-Butadiene Rubber
PmT	Poly (*m*-toluidine)
PO	Propyleneoxide Rubber
PoT	Poly (*0*-toluidine)
PS	Polymer-based Sulphur
PβN	Phenyl B Naphthyl amine
RRIM	Rubber Research Institute Malaysia
RS	Rhombic Sulphur
RSS	Smoke-Dried
RVNRL	Radiation Vulcanised Natural Rubber Latex
SBR	Styrene Butadiene Rubber
SCR	Standard Cambodia Rubber
SEV	Semi-Efficient Vulcanization
SMR	Standard Malaysia Rubber
SR	Synthetic Rubber
STR	Standard Thailand Rubber

SVR	Standard Vietnam Rubber
TBzTD	Tetrabenzylthiuram disulphide
TESPT	Bis-(3-triethoxysilylpropyl)-tetrasulfane
TMQ	Trimethylquinoline
TMTD	Tetramethylthiuram Disulphide
TMTM	Tetramethylthiuram Monosulphide
TPO	Thermoplastic Polyolefin
TPU	Thermoplastic Polyurethane
TSR	Technical Standard Rubber
VTES	Vinyl-Triethoxysilane

LIST OF SYMBOLS

Symbol	Description
M_H	Maximum torque
t_{s2}	Scorch time
t_{90}	Optimum cure time
^oC	Degree celcius
%	Percentage
wt %	Weight percentage
phr	Part per hundred rubber
Kc	Kilo cycles
Kg	Kilo gram
kN	Kilo Newton
m	Meter
dNm	Deci Newton Meter
CB-A	Chain breaking acceptor
CB-D	Chain breaking donor
R^o	Alkyl radical
ROO^o	Alkylperoxy radical
RH	Polymer chain
M100	Modulus at 100 % strain
M300	Modulus at 300 % strain

KEGUNAAN ANTI-OKSIDA SEMULAJADI DARIPADA *ELAEIS GUINEENSIS* DAUN (KELAPA SAWIT) DI DALAM SEBATIAN GETAH ASLI

ABSTRAK

Daun kelapa sawit (*Elaeis Guinensis*) mempunyai potensi sebagai anti-oksida semulajadi (NA) yang baru dalam sebatian getah asli (NR). Pencirian mengenai NA telah dijalankan menggunakan Inframerah Transformasi Fourier (FTIR) spektroskopi analisis. Berdasarkan kumpulan berfungsi, ia boleh menjadi pengekstrakan dari daun kelapa sawit mempunyai kriteria sebagai anti-oksida dengan kehadiran kumpulan polifenolik. Ciri-ciri pematangan, sifat-sifat mekanik dan termo-oksidatif terhadap kesan sistem pemvulkanan yang berbeza pada sebatian getah asli dengan kehadiran NA telah dikaji. Tiga perbezaan siri kajian telah dijalankan. Siri pertama, kesan perbezaan sistem pematangan terhadap tervulkan NR dengan kehadiran NA telah diuji. Tervulkan NR telah dimatangkan dengan pemvulkanan lazim (CV), pemvulkanan separa cekap (SEV) dan pemvulkanan cekap (EV), bersama kehadiran NA yang telah diperolehi daripada ekstrak daun kelapa sawit. Keputusan yang diperolehi menunjukkan bahawa NA adalah lebih ketara di dalam sistem SEV untuk tervulkan NR berbanding dengan sistem CV dan EV kerana mempunyai keputusan sifat mekanikal yang lebih baik, ketumpatan sambung silang dan ciri-ciri pematangan yang sederhana apabila terdedah kepada proses penuaan. Dalam siri kedua, kesan tempat asal getah asli bagi tervulkan NR bersama-sama kehadiran NA telah dikaji. NR yang berasal dari Malaysia (SMR CV60), Thailand (STR 5L), Vietnam (SVR 3L) dan Kemboja (SCR L) telah digunakan di dalam kajian ini dengan pematangan sistem SEV. Getah asli yang diperolehi daripada tempat yang berbeza menunjukkan ciri-ciri pematangan dan sifat-sifat termo-oksidatif yang setanding disebabkan oleh persamaan struktur semualajadi NR STR 5L yang

mempunyai berat molekul yang tinggi dan kandungan protein yang rendah menunjukkan sifat modulus dan kitaran hanyat lesu yang tinggi oleh pembentukkan penghabluran yang lebih banyak dengan kurangnya peluang oleh protein untuk menjadi *denatured* dalam vulkanizat NR. Kesan tervulkan NR dan getah tiruan dengan kehadiran NA telah disiasat dalam siri ketiga. Keputusan menunjukkan bahawa SBR mempunyai pretasi yang lebih baik terhadap penuaan untuk ujian sifat pengekalan dan set mampatan disebabkan oleh kurangnya reaktif ikatan kembar kepada serangan oksigen dan suhu penuaan SBR yang tinggi kerana memiliki kestabilan haba yang lebih baik berbanding NR. Sebagai kesimpulan untuk keberkesanan NA dalam sebatian getah, keputusan terkumpul dari perbandingan NA dan TMQ menunjukkan bahawa tervulkan NA telah memaparkan keputusan yang setanding dengan TMQ dalam hampir semua ujian ciri-ciri pematangan, sifat-sifat oksidatif-thermo, kitaran hayat lesu dan juga set mampatan bagi ketiga-tiga siri.

UTILASATION OF A NATURAL ANTIOXIDANT FROM *ELAEIS GUINEENSIS* (OIL PALM) LEAVES IN RUBBER COMPOUNDS

ABSTRACT

Oil palm (*Elaeis Guineensis*) leaves has the potential as a new type of natural antioxidant (NA) in natural rubber (NR) compound. Characterisation of NA was determined using Fourier Transform Infra-Red (FTIR) spectroscopy analysis. Based on functional groups, it can be shown that extraction from oil palm leaves possesses the criterion as an antioxidant with the present of polyphenolic groups. The curing characteristics, mechanical properties and thermo-oxidative studies on the effectiveness of NA in NR vulcanizate were investigated. Three different stages of investigators were performed. In the first series, the effect of different vulcanization system on NR vulcanizate in the presence of NA was studied. NR vulcanizate were cured with efficient (EV), semi-efficient (SEV) and conventional (CV) system with the presences of NA that was obtained from oil palm leaves. The obtained results have indicated that NA was more significant in SEV system for NR vulcanizate compared to CV and EV systems due to better mechanical properties, moderate crosslink density and curing characteristic results when exposed to aging process. In the second series, the effect of NR origin on NR vulcanizate in the presence of NA was studied. The NR from Malaysia (SMR CV60), Thailand (STR 5L), Vietnam (SVR 3L) and Cambodia (SCR L) were used in this study and cured using SEV. The origin of NR showed comparable curing characteristics and thermo-oxidative properties due to the same NR structure. NA STR 5L possesses higher molecular weight and lower extractable protein content exhibiting higher modulus and fatigue life cycle by inducing more strain crystallization and possesses less protein being denatured in NR vulcanizate. The effect of natural and synthetic rubber

vulcanizate in the presence of NA was investigated in the third series. The results show that SBR has performed better on aging for retention and compression set testing due to the less reactive double bond to oxygen attacked and it has higher aging temperature as it has better heat stability compared to NR. As a conclusion for effectiveness of NA in rubber compounds, accumulated results from the comparison of NA and TMQ shown that NA vulcanizate has presented comparable results with TMQ in almost all curing characteristics, thermo-oxidative properties, fatigue life cycle and compression set testing for all three series.

CHAPTER 1

INTRODUCTION

1.1 Preface

Natural rubber (NR) is an elastic hydrocarbon polymer produce from the latex of the *Hevea Brasiliensis* tree. *Hevea Brasiliensis* almost becoming the almost only commercial source of NR due to the capacity of producing large amounts of high quality rubber (van Beilen and Poirer, 2007). Natural rubber will crystallize upon straining. Strain-induced crystallization imparts outstanding green strength, tack and high resistance to deformation. These elasticity properties give the fact that all rubber is composed of long and flexible molecules which is linear high polymer (Matthew, 2007). In 1839, Hancock and Charles Goodyear had discovered about the remarkable resistance of 'vulcanized' rubber which was form from the combination of sulfur dust, heat and raw rubber (Yam, 2007). In addition, the long molecules in rubber need to become crosslinked by vulcanization to obtain strong and flexible properties. Generally, under rubber processing, mastication process must be added to soften the rubber by partly broken the long polymer chain before rubber compounded easily with other ingredients, such as, fillers; antioxidants; accelerators; vulcanizing agents; and plasticizers. The compounded rubber was sheeted, shaped, and vulcanized accordingly to the given applications (http://www.infoplease.com/encyclopedia/science/rubber-natural-rubber.html, 14/07/2014).

It is well known that natural rubber is the most popular rubber due to their unique and outstanding properties. However natural rubber has limitation where it will become aged after it has been used for a long period of time especially in outdoor applications. It does not only affect the material properties but also the lifetime of natural rubber (Yeong et al, 2005). Due to the presence of double bond in natural rubber structure which is easily been attacked by solvents, oxygen, ozone, humidity as well as UV rays, natural rubber is highly vulnerable to degradation. According to Datta and Huntik, (2008), when natural rubber is completely oxidized, it would become hard and brittle because the chemical mechanism between natural rubber crosslinking and oxygen molecules has started to dominate again.

Antioxidant, either natural or synthetic, can be used to reduce the rate of degradation process by reacting with free radical that is formed by oxidation. This reaction leads to the formation of oxidative cross-linked layer which causes reduction to the rate diffusion by oxygen into the interior natural rubber compound (Li et al, 2003). Thus, for natural rubber cases, antioxidants are desperately needed in compounding for better protection from ageing and natural antioxidant become an additional benefit which is in accordance to the interest of producing green products.

1.2 Problem statement

In most rubber application, synthetic antioxidants are added into rubber compounding to prevent the degradation process from occurring during usage. For all this time, synthetic antioxidants frequently meet the requirement for all products including food, rubber, polymers, elastomers fats and oils and also lubricating oils. But in several countries there have been some restrictions about the use of synthetic antioxidant which cause undesirable effect on environment and human health (Knez et al, 2003). Among the synthetic

antioxidants types, butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are the antioxidants that are most commonly used to prevent the degradation process. There was a report mentioned BHA and BHT could be toxic and dangerous beside the higher manufacturing cost and low efficiency (Nunez et al, 2001).

Thus, in order to tackle this kind of problem, research on developing a new type of antioxidants for rubber compounds has gained interest among academia and industries towards natural resources. These growing interests in green technology have led to the substitution of synthetic antioxidant with natural antioxidant. Natural antioxidant can prevent thermo-oxidative degradation of rubber without causing any environmental pollution. Accordingly, for the purpose of this research, natural antioxidants (NA) from *Elaeis Guineensis* (oil palm) leaves were used as antioxidant in preparing natural rubber compound. The leaves of the oil palm have been identified as a good natural source of phenolic compounds which is an important criterion for good antioxidants (Anandhan et al, 2011). The phenolic compounds are known for trapping the free radical to prevent oxidative degradation.

On the other hand, Malaysia as the second largest producer and exporter of palm oil in the world after Indonesia generates a significant amount of oil palm leaves waste. In a year, about 30 leaves were produces by a young tree and 20 leaves by established trees that already over 10 years (MPOC, 2008). Because of this, the mill will have generally excess leaves which are not used and need to be disposed off separately. Thus, these waste oil palms leaves can be extracted in order to produce as an antioxidant in natural rubber (Kawser and Nash., 2000).

1.3 Objectives

The effects of natural antioxidant were studied using different vulcanization system, different origin of natural rubber and different type of rubber vulcanizate. The main aims of this research are:

- To produce natural antioxidant from oil palm leaves (OPE) by using solvent extraction method.
- To investigate the effect of three different vulcanization systems in the presence of natural antioxidant from OPE on cure characteristic, mechanical properties and ageing resistant of natural rubber vulcanizates and compare the effectiveness of natural antioxidant with TMQ.
- To investigate the effect of four different natural rubber origins in the presence of natural antioxidant from OPE on cure characteristic, mechanical properties and ageing resistant of natural rubber vulcanizates and compare the effectiveness of natural antioxidant with TMQ.
- To study the effect of natural antioxidant cure characteristic, mechanical properties and ageing resistant of natural and synthetic rubber and compare the effectiveness of natural antioxidant with TMQ.

1.4 Organisation of the thesis

This research thesis has been divided into five chapters which are introduction, literature review, methodology, results and discussion and also conclusion.

- **Chapter one** - This chapter describes the preface of this research title, problem statement and also the objectives of this research. This chapter will give the early introduction before going into the details explanation in other chapters.

- **Chapter two** – This chapter explain more about the researches that had already been done by previous researchers.
- **Chapter three** – In this chapter, the methodology of this research has been explained step by step. Starting from the raw materials, compounding, processing until the testing that had been conducted. Besides, this chapter also mentioned about the three main series which had been investigated in this research.
    - First series: In this series, the effect of natural antioxidant will be investigated on different vulcanization system. The natural rubber compound is being prepared in three different formulations according the vulcanization system which are conventional vulcanization (CV), semi-efficient vulcanization (SEV) and efficient vulcanization (EV).
    - Second series: In this series, different origin of natural rubber is being used to investigate the effect of natural antioxidant. The natural rubber from Malaysia (SMR CV60), Thailand (STR 5L), Vietnam (SVR 3L) and Cambodia (SCR L) have been prepared by using same vulcanization system where already been notified as a good vulcanization system which gave a good effect with natural antioxidant.
    - Third series: In this series, two types of rubbers which are natural and synthetic rubber are being prepared to investigate the effect of natural antioxidant. SMR CV60 as a natural rubber and SBR for the synthetic rubber.

  For each part of this series, the curing characteristics, crosslink density, mechanical properties (tensile strength, elongation at break, tensile modulus at 100 % and tensile modulus at 300 %, tear strength), fatigue life and compression

set were carried out. In addition, thermo-oxidative aging were also conducted to explain more about the influence of antioxidant in rubber vulcanizate.

- **Chapter four** – This chapter will cover the results and also the discussion. The results will be discussed accordingly to the series for deeper understanding. At the end of each series, the comparison between NA and TMQ will be discussed in order to see the effectiveness of NA in rubber vulcanizates.
- **Chapter five** – For this chapter, all the statement, results and discussion will be concluded as a conclusion. This conclusion will show whether or not the objectives of this research have been achieved.

CHAPTER 2

LITERATURE REVIEWS

2.1 Natural Rubber (NR)

The most important elastomer that is available and had been used in rubber product today is natural rubber (NR). Figure 2.1 has shows the latest Malaysia's rubber consumption by type from 2000 until 2013. NR already becomes more attractive compared to synthetic rubber as a renewable resource with better elasticity, flexibility, long lasting and insulating of its properties. With these useful properties, thousands of products can be produced in rubber industry (Klingensmith and Rodger, 2004).

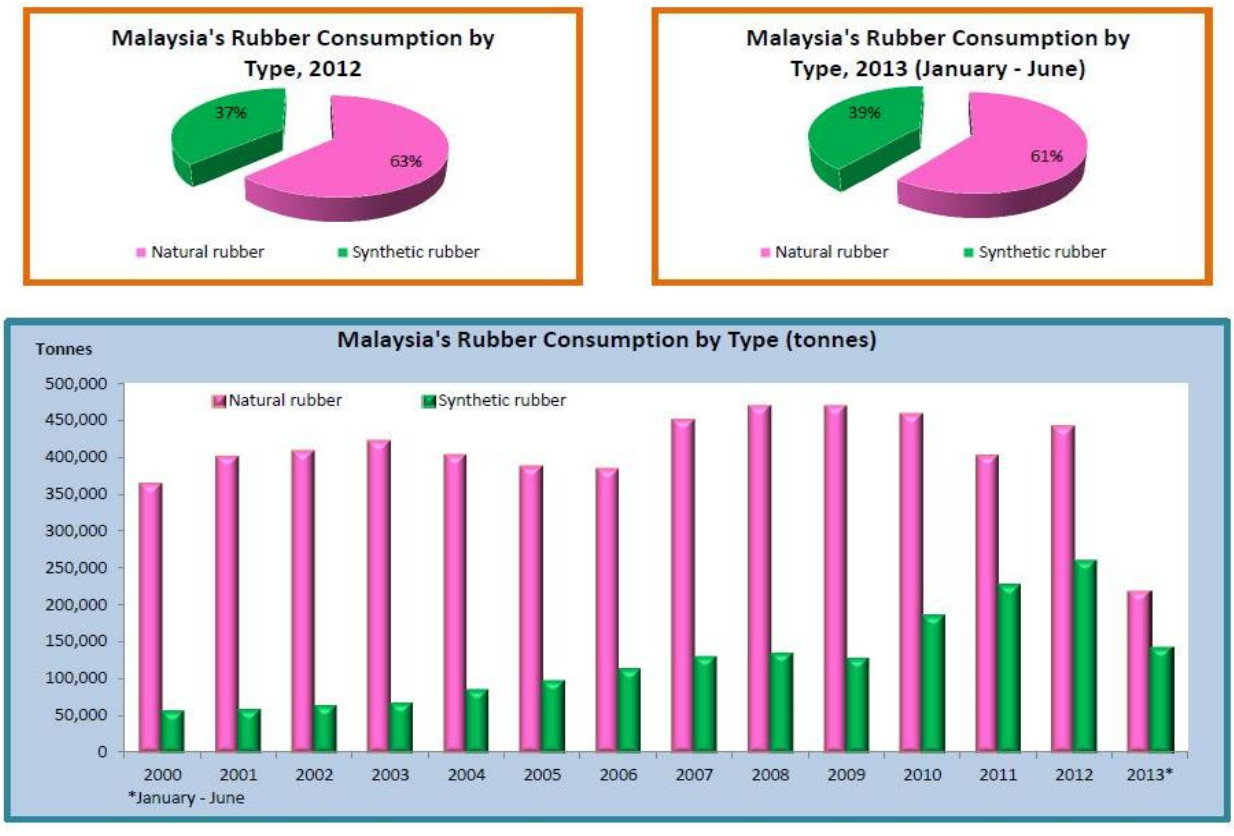


Figure 2.1: Malaysia's rubber consumption by type (tonnes)

(http://www.lgm.gov.my/nrstat/nrstats.pdf, 10/01/2014)

In Malaysian federation about 12 of 14 states of rubber growing areas are located at Peninsular Malaysia and the rest are located at East Malaysia. Altogether Malaysia produces almost 20 % of the world's natural rubber. Malaysian rubber has gone to every country in the world and is recognized to be the best but reaching the year to 2013, the production of NR has dropped from 922, 798 tonnes to 394, 238 tonnes (http://www.lgm.gov.my/general/NRHistory.aspx, 10/01/2014). To overcome this problem, Malaysia's scientist has outcome with scientific cross breeding and careful cultivation on the newer varieties of rubber trees. Thus, NR production is expected to rise in the coming years. Figure 2.2 and Figure 2.3 has shown the statistics of Malaysia's NR production and Malaysia's trade in rubber products.

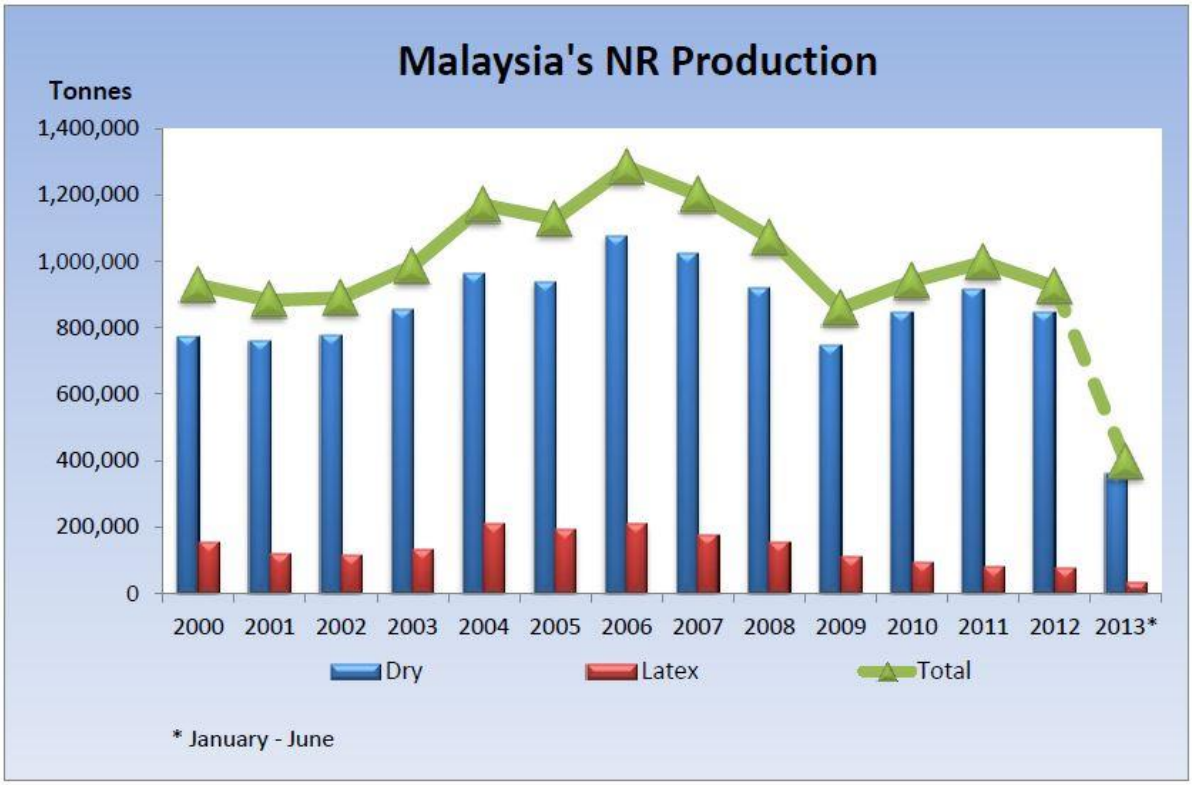


Figure 2.2: Malaysia's NR production for 2000 until 2013

(http://www.lgm.gov.my/nrstat/nrstats.pdf, 10/01/2014)

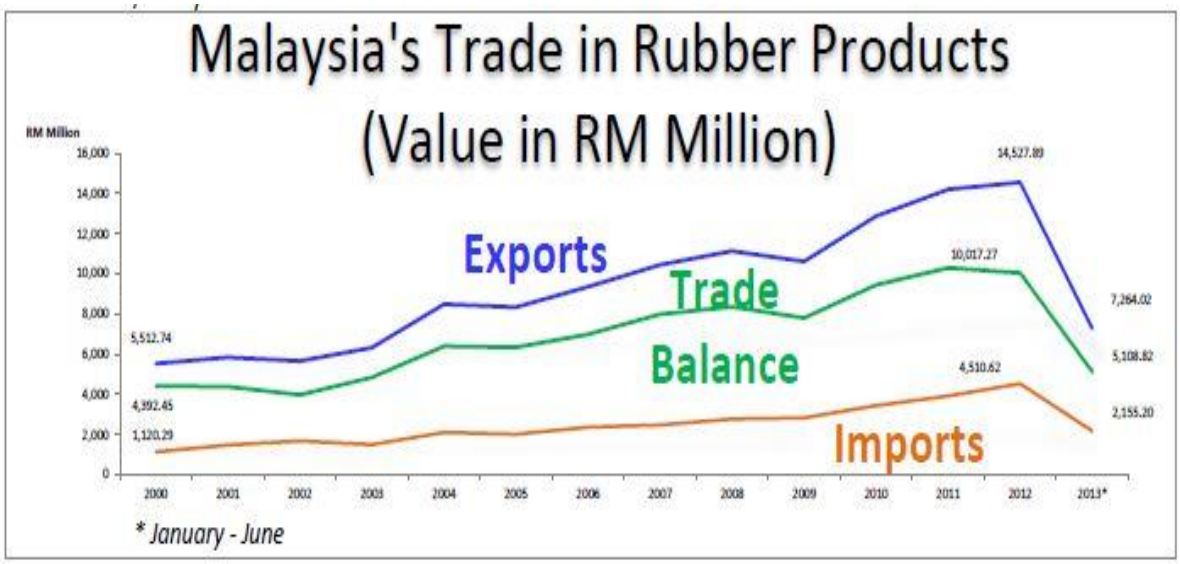


Figure 2.3: Malaysia's trade in rubber products for 2000 until 2013

(http://www.lgm.gov.my/nrstat/nrstats.pdf, 10/01/2014)

NR are unsaturated, contains double bonds which interpretations for its outstanding viscoelastic properties (Mark and Erman, 2005). Eventhough NR possesses an attractive range of properties, possessing excellent mechanical properties and good processing characteristics, NR has limitation. Due to the presence of double bonds in the main chain, NR is highly exposed to degradation. Heat, humidity, light, ozone, radiation are the main source accelerating the degradation of NR (Arayapranee and Rempel, 2008).

Many researches had been done in order to improve the properties of NR at a time to sustain the NR's production for the future undertaking. Among the researchers, there was grafting of cardanol on to NR in the latex stage. Mohapatra and Nando (2014) had used cardanol which is a phenolic lipid obtained from anacardic acid, cashew nutshell liquid (CNSL), a byproduct of cashew nut processing as a green substitute for aromatic oil as plasticizer in NR. The cardanol grafted natural rubber (CGNR) has resulted 45.6 % increment on the NR molecular weight without affecting the molecular weight distribution. It was also

found to have lower Mooney viscosity, lower Wallace plasticity number, higher cure rate, better physico-mechanical properties, better flow behavior and exhibit lower glass transition as compared to the unmodified natural rubber (Mohapatra and Nando, 2014). Furthermore, since 2010, the interests of NR researchers on the useful of epoxidized NR (ENR) in NR compounding are still growing. ENR has reported to have better properties compared to NR on oil resistance, damping, fatigue behavior and also gas permeability. Moreover, epoxidation are known as an efficient method for introducing the reactive group and polarity towards polyisoprene backbone (Fernandes et al, 2011)

2.1.1 Origin of NR

In early economies, NR latex comes from rubber tree types *Ficus elastica, Funtumia, Castilloa elastica, Landolphia owariensis, Palaquium oblongifolium* and *Manihots* plants, but after a while they were displaced by NR latex from rubber trees (*Hevea brazilenses*) which are grown in the southern equatorial region of America. The latter from *Hevea brazilenses* trees give a greater yield of superior elastic properties towards NR latex (Hoffman, 1989). Figure 2.4 shows several types of rubber leaves. In 1876, it was brought to India and Asia region especially Malaysia, Indonesia, Thailand, Vietnam and also Cambodia for the cultivation of rubber trees (Loadman, 2005). It seems more like milk but its consists of cis-1,4 polyisoprene (Rattanaphan, 2012).

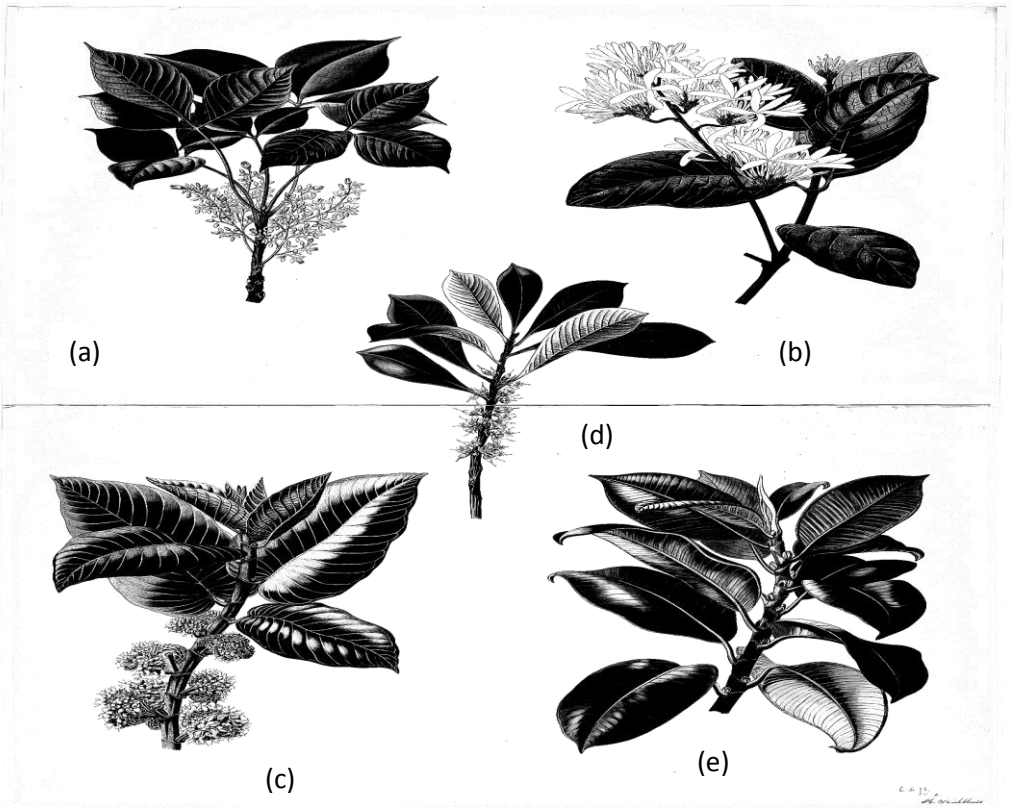


Figure 2.4: (a) *Hevea Brazillines*, (b) *Landolphia owariensis*, (c) *Castilloa elastica*, (d) *Palaquium oblongifolium and* (e) *Ficus elastic* (Schilthuis, 1960)

Generally, solid NR latex contains neutral lipids (2.4%), glycolipids and phospholipids (1.0%), proteins (2.2%), carbohydrates (0.4%), ash (0.2%), and other compounds (0.1%) (Sentheshanmuganathan, 1975; Nair, 1987). Normally, the latex is diluted with water to a solid content up to 12 to 18 % and it would require more acid for coagulation process if more latex is diluted. This is because the coagulum changes their properties in air under influence of bacteria. After been coagulated with formic acids and pressed to consolidate the rubber between rollers, the rubber went to air-dried (ADS) or smoke-dried (RSS) (Sakdapipanich, 2007). These are the two ways of processing the coagulum; ADS where the crepe prepared by coagulating the latex, washing, pass through a series of rolling and air-dried for a few days; and RSS where prepared as similar with ADS but drying by exposed to hot wood smoke (Hoffman, 1989; Blow and Hepburn, 1982).

In 1965, Malaysia had developed new scheme, which is known as the Standard Malaysia Rubber (SMR) and also embraced by other countries like Indonesia (SIR), Thailand (STR) and Vietnam (SVR). Today, it has been classified as Technically Specified Rubber (TSR) where the rubber is supplied in compact, bale or block form and mainly graded by dirt content (% wt) (Sakdapipanich and Rojruthai, 2012). The TSR scheme consists of following grades and Figure 2.5 shows the specification scheme for TSR with different grades:

- TSR CV – constant viscosity of latex

-TSR L – light coloured from latex

-TSR 5 – Equivalent to 1 RSS from sheets

-TSR 10 – Field grade material

-TSR 20 – Base field grade material

		TSR CV		TSR L	TSR 5		TSR 10		TSR 20	
Parameter	Unit	SMR CV50	SMR CV60	SMR L	SMR 5*	SMR GP	SMR 10	SMR 10CV	SMR 20	SMR 20CV
Dirt (max)	% wt	0.02	0.02	0.02	0.05	0.08	0.08	0.08	0.16	0.16
Ash (max)	% wt	0.50	0.50	0.50	0.60	0.75	0.75	0.75	1.00	1.00
Nitrogen (max)	% wt	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile Matter (max)	% wt	0.80	0.80	0.50	0.80	0.80	0.80	0.80	0.80	0.80
Po (min)	% wt	NA	NA	35	30	NA	30	NA	30	NA
PRI index (min)		60	60	60	60	50	50	50	40	40
Lovibond Color: individual value (max)		NA	NA	6.0	NA	NA	NA	NA	NA	NA
Lovibond Color: range (max)		NA	NA	2.0	NA	NA	NA	NA	NA	NA
Mooney Viscosity (ML, 1+4, 100°C)		50 +/- 5	60 +/- 5	NA	NA	65 +7/-5	NA	60 +7/-5**	NA	65 +7/-5**

Figure 2.5: Specification scheme of Standard Malaysia Rubber (SMR) with various grades

(www.astlettrubber.com, 25 June 2013)

2.1.2 General purpose of NR

Generally, NR composed of along chains of isoprene which randomly entangled and the typical range of NR molecular weight is 1,300,000 which include 60% of the molecules. NR is a polymer of isoprene, usually cis-1, 4-polyisoprene (Kothandaraman, 2008). The repeating unit of isoprene can have different stereoregularity of cis- and trans- configuration which is essential for elasticity. This cis-configuration indicates the chain extensions on the ethylene double bond occur at the same side of the ethylene double bond meanwhile trans-configuration indicates the opposite sides (Kauffman and Seymour, 1990).

NR possess superior in building tack and it also can deformed in a reversible manner, which is a significant characteristic of its elastic behavior but when NR is cooled very slowly around -35 ^{o}C, it becomes opaque and loses it elasticity due to a partial crystallization. In addition, even without reinforcing filler added in crosslinked NR, it still has higher tensile strength compared to synthetic rubbers (Hoffman, 1989). NR also has high resilience, good tear resistance and high fatigue to failure in cured state. Figure 2.6 shows general repeating unit of polyisoprene of NR in cis-configuration.

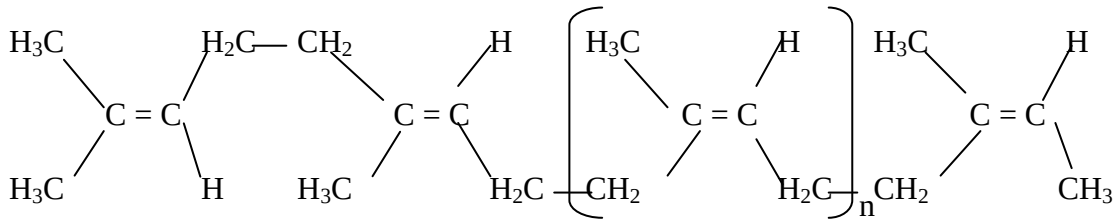


Figure 2.6: Chemical structure of cis-1,4 polyisoprene from NR (Herculano et al., 2011)

2.2 Synthetic rubber

The synthetic rubber (SR) is obtained by polymerizing certain organic compounds which may have properties similar to rubber and some desirable properties. Most of these are derived from butadiene derivatives and contain carbon-carbon double bonds. The SR are obtained through homopolymers of 1, 3 butadiene or copolymer in which one of the monomers is 1, 3 butadiene or its derivative so that the polymer has the availability of double bonds for its vulcanization. This type of SR can be produced by vinyl polymerization, by polycondensation as well as by polyaddition reactions (Ebelewe, 2000).

2.2.1 Type of synthetic rubber

For chemical industry, SR types has grown bigger and it has become useful if classify the SR with different grades. Thus, the types of SR were differentiating according ASTM D 1418 (1994):

(i) The main ones with 95 % share at total market - Isoprene rubber (IR), styrene-butadiene rubber (SBR), butadiene rubber (BR), chloroprene rubber (CR), acrylonitrile-butadiene rubber (NBR), ethylene-propylene-diene rubber (EPDM), butyl rubber (IIR).

(ii) Specialty rubber - epoxidize NR (ENR), urethane rubber (AU), epichlorohydrin rubber (ECO), polyglycol ether (OT), thermoplastic polyurethane (TPU), thermoplastic polyolefins (TPO), etc and

(iii) Lesser importance or merely interest – vinylpyridine-butadiene rubber (PBR), propyleneoxide rubber (PO), acrylonitrile-chloropene rubber (NCR), acrylonitrile-isoprene rubber (NIR), styrene-isoprene rubber (SIR), styrene-chloropene rubber (SCR), etc

2.2.1.1 Styrene-butadiene rubber (SBR)

SBR can be considered as a general purpose rubber, same as NR or IR, since it can be used in many applications of rubber products. SBR has about 23 – 40 % of styrene and the ratio of butadiene to styrene is mostly 76.5 to 23.5 % by weight. Figure 2.7 shows the copolymer composition of SBR. Lower viscosity of SBR gives higher extrusion rate, easily to mill and shows less heat generation during mixing while higher viscosity SBR have better green strength, less porosity and accept higher filler and oil loadings. Increasing the molecular weight of SBR, the higher resilience can be achieved and also improved in mechanical properties; tensile and compression set (Hoffman, 1989).

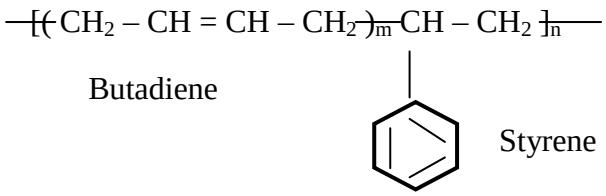


Figure 2.7: Chemical structure of styrene-butadiene rubber (SBR) (Omprakash, 2012)

Compared to NR, SBR still inferior in tear resistance and elastic properties but particularly advantageous in abrasion resistance, aging resistance, durable and has higher heat built up. For aging resistance, SBR which has 20 ^{o}C higher service temperature than NR makes it become more resistant to heat compared to NR. However, without antiozonants, SBR is still non-resistant to weathering and ozone degradation the same as NR (Hoffman, 1989). SBR applications usually involved combination with other rubbers like BR, NR or IR and general purpose of SBR is in tires industry. Other applications are belting, shoe soling, cable insulation, hose, sanitary products, food packaging, etc.

Nowadays, SBR is widely used in composite field. For example in tire industry, in command to improve chemical reaction between SBR and silica composite, grafted polymerization of vinyl-triethoxysilane (VTES) onto SBR was carried out in latex using potassium peroxydisulfate (KPS) as initiator. This SBR-g-VTES / silica composite exhibited higher tensile strength, hardness and wet skid resistance compared to SBR / TESPT / silica composite whereas bis-(3-triethoxysilylpropyl)-tetrasulfane (TESPT) is used as silane coupling agent (Yin et al., 2012). Other than that, liquid rubber / clay master batch also was introduced as one of the important role to improve the filler-matrix interaction which was first prepared using a high-speed centrifugal mixer and then compounded with neat SBR using conventional rubber compounding equipment. These approaches give better results in clay dispersion with rubber matrix and improvements in tensile strength and elongation at break (Fang et al., 2013).

2.3 Rubber compounding ingredients

There are numerous chemicals and additive that can be used in rubber compounding in order to achieve excellent properties for possible applications. All ingredients have specific roles and influence towards the end properties of rubber compounds. However, these properties might also be significantly modified by the amount of the ingredients used. In short, Dick (2001) has summarized rubber compounding as the science of art in selecting the quantities of remarkable compounding ingredients to mix together and producing useful rubber formulation that is processable to meet or exceed the final product requirement from customer which can be competitively priced.

2.3.1 Vulcanizations agent

A vulcanization agent is one of the important ingredients in rubber compounding. This is because; vulcanizing agent induced chemical reaction between rubber molecular chains to crosslink with one another forming network linkages (Barlow, 1993). By crosslinking, the rubber behavior changes from thermoplastic to elastic state. This is because, more crosslinking causes the rubber chain becomes tighter and need a lot of forces to deform (Hofman, 1989).

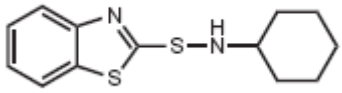
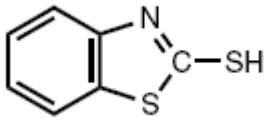
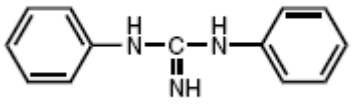
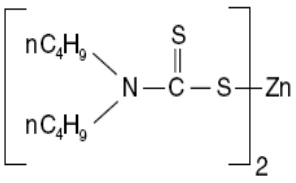
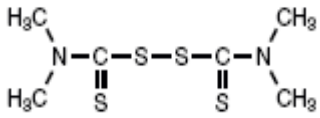
The mechanism of vulcanization and the chosen vulcanizing agent is depends on the structure and type of rubber used in the compounding (Gonzales et al., 2005). For example, the diene-rubbers like NR, SBR, NBR, etc. can be vulcanized with sulphur or peroxides. Because of easier adjustment, higher flexibility, better mechanical properties and less economical reason, sulphur is the most preferred agent compared to peroxide. The addition of accelerator and activator to sulphur, thermally stable covalent bonds are formed between the carbon-carbon double bonds of elastomer chains (Yam, 2007). White and De (2001) also shared that due to the softening of the rubber by heat, there is an increase number on study on the development of vulcanization with sulphur. Sulphur known as one of the curing agent for elastomer that could result in less heat-sensitive product but dimensionally more stable. Organic peroxide also is used as crosslinking agents with natural rubber, polybutadiene, and its copolymer.

Generally, commercial rhombic sulphur which is originated from natural sources is widely used in rubber industry but nowadays, there has been an interest to research on the use of sulphur from petroleum refinery by-products. In order to increase the value of by-product of petroleum refining which usually been sold at low cost for the production of sulfuric acid, the comparative study between commercial rhombic sulphur (RS) and petroleum-based sulphur (PS) was conducted by Pangamol et al., (2013) on their report with title 'Effectiveness of By-product Sulfur from Petroleum Refining as a Rubber Vulcanizing Agent: A XANES Investigation'. The results show that PS and RS have similar chemical structure in vulcanized rubber which approach to have comparable results for the mechanical properties of various type of rubber. In other words, PS has a strong possibility to be used as vulcanizing agent in the rubber industry (Pangamol et al., 2013).

2.3.2 Accelerators

The use of accelerator, an organic chemical that is applied to speeds up the rate of vulcanization is also important in modern rubber compounding. Yam (2007) stated that accelerator is divided into 5 classes according to their structure application in rubber field which had already been summarized at Table 2.1.

Table 2.1: Classes of accelerator (Yam, 2007)

Class	Description	Example
a) Sulfenamides	- Primary accelerator - Provide longer scorch time which avoids premature crosslinking	 N-cyclohexylbenzothiazole-2-sulfenamide (CBS)
b) Thiazoles	- Moderate vulcanization rate & scorch time - Can used alone or combine together with other accelerators	 2-mercaptobenzothiazole (MBT)
c) Guanidine	- Secondary accelerator - Used with Thiazoles class for technical good	 N,N'-Diphenylguanidine
d) Dithiocarbamates	- Faster than Thiurams class - Act as ultra-accelerator	 Zinc Dibutyldithiocarbamate
e) Thiurams (others than sulfides)	- Act as ultra-accelerator with normal amount of sulphur	 Tetramethylthiuram disulphide

According to Gonzalez et al., (2005), the amount of sulfenamide accelerator used and its efficiency working with sulphur in rubber compounding can improve the vulcanization rate and crosslink concentration. This is because the type of crosslink formed depends on sulphur / accelerator ratio and it will be explained in Figure 2.4.

Over the last century or so, the very common traditional accelerators such as tetramethylthiuram disulphide (TMTD) have been found in rubber articles before it was reported that TMTD are carcinogenic because of the production of nitrosamines during heating for the vulcanization reaction (Vieira et al., 2006). Other accelerators which form the hazardous nitrosamines are tetramethylthiuram monosulphide (TMTM), N-oxydiethylene dithiocarbamyl N^{l}-oxydiethylene sulphenamide (OTOS) and N-oxydiethylene–2-benzothiazole sulphenamide (MBS) (Forrest, 2006). Because of these report, recent research are focusing on finding a safer substitute to these hazardous accelerators. In Abhitha and Kurian., (2013), they had proposed tetrabenzylthiuram disulphide (TBzTD) to be a safe non-carcinogenic accelerator in rubber vulcanizates. The tests of TBzTD show a comparable crosslink density and improved in aging resistance. These indicate that TBzTD can be used as a safe accelerator in rubber field (Abhitha and Kurian, 2013).

2.3.3 Activators

The modern recipe of rubber compound between accelerator and activator; zinc oxide and fatty acid (e.g: stearic acid) improve vulcanization system with a good crosslinking. Zinc oxide reacts with stearic acid to form zinc stearate which speed up the rate of sulfur vulcanization. It is believed that zinc stearate give a salt that form intermediate complexes with the accelerators. The complexes give more effective in activating the sulphur vulcanization process, thus increasing the reaction rate (Niyogi, 2007).

Parallel to the requirements for environment protections, recent research about organic zinc compound (zinc resinate) in rubber technologies has been projected as a substituent of harmful zinc oxide. As far as physico-mechanical properties are concerned, zinc resinate has been found to have slightly lower compared to zinc oxide but the differences getting smaller at the higher amounts of zinc resinate. Meanwhile, when there are requirements for non-toxic or environmentally friendly of rubber compounds, zinc resinate comes as an appropriate solution (Todorova et al., 2012).

2.3.4 Antioxidants

The inhibition of oxidation in polymer during fabrication and processing is very important to ensure the long-term stability of the polymer when it is subjected to various environmental conditions. Thus, antioxidants have been designed to be added into the polymer to reduce oxidation since it's able to absorb the oxygen and other foreign molecules which can slow down the oxidation process and the mechanism can been seen in Figure 2.8. Rodgers (2004) stated that typically, antioxidant is an external component substance added in small quantities to extend the service life of hydrocarbons. This can prevent the material from susceptible to oxidation since antioxidant reacts with oxygen and reacts with free radical that degrades vulcanized rubber. This protection is expected to continue through the storage period prior to utilization in a fabrication step.

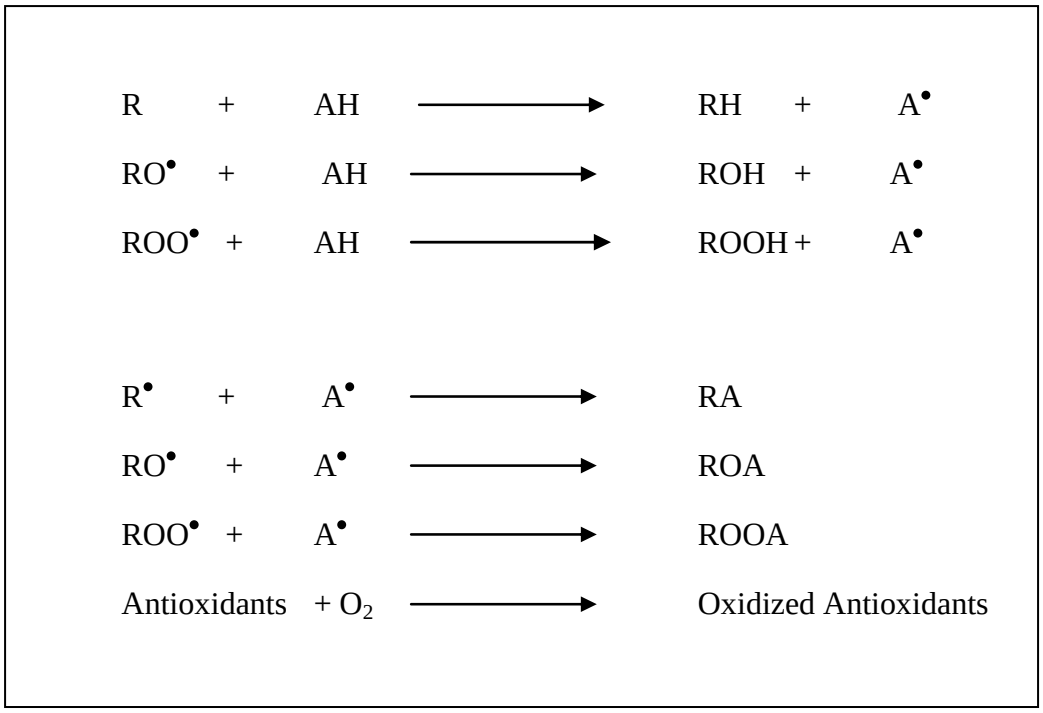


Figure 2.8: Mechanism of antioxidants (Brewer, 2011)

According to Pritchard (1998), two main types of antioxidants are classified by the way their act in the overall oxidation process: the chain breaking which usually disrupted the primary oxidation cycle and the preventive antioxidants that retard the formation of free radicals in initiation step (Pritchard, 1998). In addition, as secondary antioxidants; alkyl and alkyaryl, the preventive antioxidants destroy the hydroperoxides first before they can decompose into radicals to protect the raw elastomer in storage but during vulcanization, they usually destroyed (Rodriguez and Touchet, 1998). Generally, all antioxidants perform in a particular way to protect polymers and rubber compounds from oxidation. Thus, it is essential to understand the mechanism of various antioxidants before applying them in any experiments (Sung, 2004).

2.3.4.1 Chain breaking antioxidants

As reported by Vitarelli et al., (2002), the chain breaking antioxidants are those identified as primary antioxidant usually scavenges the radicals before they can react with the elastomer and they generally classified as below; (a) phenolic antioxidant and (b) aromatic amine antioxidant. Phenols are commercially available as pure chemicals. However, according to Chanda and Roy (2007), aromatic amines are more powerful antioxidants compared to phenols but have limitation due to the staining properties. The stabilization of chain breaking antioxidants is referred below;

Stabilization reaction

Chain breaking acceptor antioxidants (CB-A) are antioxidants which are able to compete with oxygen for alkyl radicals ($R^{\cdot}$). According to Abad et al (2002), ($R^{\cdot}$) are removed from auto-oxidizing system in competition with chain propagation reaction and are only effective under oxygen deficient condition, as shown in reaction 1.

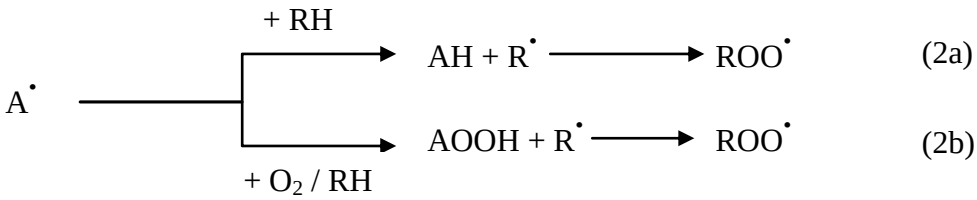
$$Q + R^{\bullet} \xrightarrow[O_2\text{-deficient}]{\text{CB-A}} \text{Non-radical products} \quad (1)$$

Chain breaking donor antioxidants (CB-D) are electron or hydrogen atom donors which are capable of reducing alkylperoxy radicals ($ROO^{\cdot}$) to ROOH, as shown in reaction 2.

$$AH + ROO^{\bullet} \xrightarrow{\text{CB-D}} ROOH + A^{\bullet} \longrightarrow \text{Non-radical products} \quad (2)$$

Propagation reaction

Antioxidant radical ($A^{\cdot}$) formed from reaction 2 does not continue the kinetic chain either by hydrogen abstraction (2a) or by reaction with oxygen (2b). This is because ($A^{\cdot}$) must be able to lead to stable molecular products rather than proceed with propagation reactions (Pritchard, 1998).



2.3.4.1 (a) Phenolic antioxidant

Phenolic compound has been identified as one of the good source which has a potential to be a good antioxidants toward rubber products. This is because phenolic compounds are excellent as hydrogen or electron donor. Their radical intermediates also relatively stable due to the resonance delocalization. Besides that, phenolic compound is lacking suitable sites to be attacked by molecular oxygens (Shahidi and Naczk, 2004). Five main phenolic compounds which are recognized as the most broadly used as primary antioxidants are shown in Figure 2.9.